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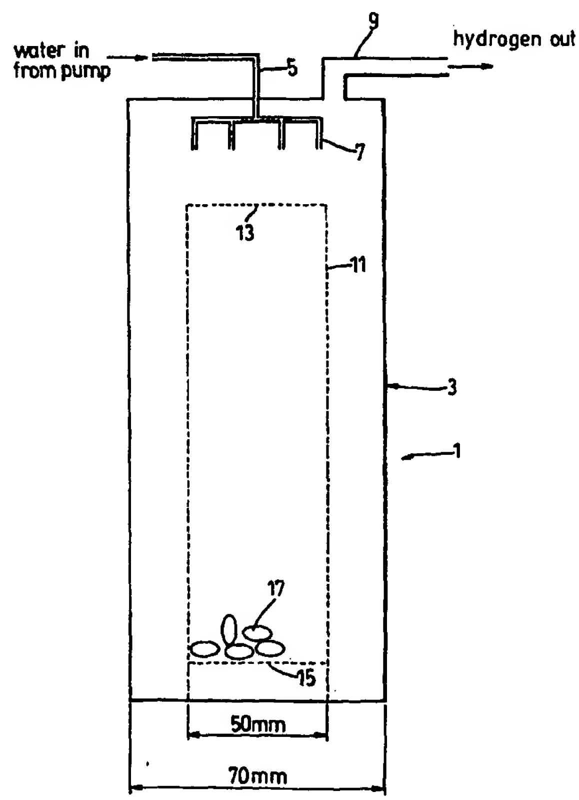
(57) Abstract

A hydrogen generating composition comprises two hydrides both capable of reaction with water to produce hydrogen. One of the hydrides is a complex hydride of a Group IA element and a Group IIIB element. The presence of the other of the hydridres results in the reaction with water of the composition being modified compared with that of the complex hydride alone with water. Apparatus for generating hydrogen using such a composition is also disclosed.



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HYDROGEN GAS GENERATION

FIELD OF THE INVENTION

The generation of hydrogen gas for use in, for instance, fuel cells or balloons is a matter of great current interest. The hydrogen gas is required to be produced efficiently, safely and with high purity.

BACKGROUND OF THE INVENTION

JP-63222001-A discloses an agent for hydrogen gas generation in the form of a complex metal hydride compound of a Group IA element and a Group IIIA element together with a transition metal compound (having a higher standard electrode potential than that of zinc ion) as well as chemicals which can soften hard water. The Group IA element may be lithium, sodium or potassium and the Group IIIA element may be boron or aluminium. The transition metal may be selected from Mn, Fe, Co, Ni, V, Cu, Ru, Rh, Pd, Os, Ri and Pt. The water softening agents may be, for instance, boric acid, boron oxide, a phosphate, a carbonate, nitrilo triacetate, oxalic acid or tartaric acid.

This publication is typical of proposals for generating hydrogen by using the so-called "hydride" group of metal salts which produce high purity hydrogen upon contact with water. Such agents have the potential to give higher storage densities, both volumetrically and gravimetrically, than conventional storage technologies such as compressed gas and rechargeable metal hydrides.

There are commercially available pellets containing sodium borohydride and a cobalt(II) chloride catalyst (7.5% by wt) which forces the hydrolysis reaction to completion.

Expansion of the reacting material is a problem frequently encountered with hydrogen generators. The product material is considerably less dense than the precursor, with a result that unreacted hydride becomes encapsulated and inaccessible to further water, thereby shortening the operating lifetime of the generator and reducing its overall energy storage density.

Hydrogen generators using sodium borohydride have demonstrated serious safety problems because of hydration of the product material ($NaBO_2.xH_2O$). The hydrolysis reaction of sodium borohydride:

$$NaBH_4 + 3H_2O \rightarrow NaBO_2\ .H_2O + 4H_2$$

liberates large quantities of heat which, unless the reaction is closely controlled, is capable of raising the reactor temperature to a point at which the bound water is released. This process results in further hydrolysis of unreacted borohydride, further heat release and so on. Hence, an uncontrollable, runaway reaction is possible.

A particular problem is caused by the fact that there is an incubation period during which there is present an excess of water. During this period the reaction proceeds only slowly until the temperature rises above about 40°C. There is then a sudden increase in the reaction rate and an accompanying temperature rise associated with the exothermic reaction. A certain delay is therefore seen between the time of water addition and the subsequent hydrogen production. However this delay is difficult to predict. In automated systems where the hydrogen pressure governs the water feed rate, water addition may continue until the pressure rises. In such cases, the reaction that then occurs can be of such violence because of the high water presence that vessel rupture due to over pressure or over temperature may occur causing injury to the operator.

STATEMENTS OF INVENTION

According to the present invention there is provided a hydrogen generating composition comprising two hydrides both capable of reaction with water to produce hydrogen, one of said hydrides being a complex hydride of a Group IA element and a Group IIIA element, whereby the presence of the other of said hydrides results in the reaction with water of the composition being modified compared with that of the complex hydride alone with water.

Preferably, the complex hydride is present in the composition in a relatively major amount compared with the other of said hydrides.

The complex hydride includes a Group IA element such as lithium, sodium or potassium and a Group IIIA element such as boron or aluminium. Examples of complex hydrides are sodium borohydride and lithium borohydride, with sodium borohydride being preferred.

The other hydride required by the composition of the present invention is typically a simple hydride such as lithium hydride or beryllium hydride, with lithium hydride being a preferred hydride.

The complex hydride may be a mixture of two or more complex hydrides and the simple hydride may be a mixture of two or more simple hydrides.

The simple hydride may be present in the composition in the amount up to 50% by wt. However it is preferably present in an amount of from 5 to 20% by wt and more preferably from 8 to 12% by wt.

The presence of the simple hydride may affect the hydrogen generating reaction in different ways. However, it is preferred that the simple hydride acts as an overall reaction initiator. Thus, the preferred simple hydride, lithium hydride, is highly reactive and, indeed, reacts preferentially with water, liberating heat and raising the temperature of the reaction medium, according to the equation:

$$LiH + H_2O \rightarrow LiOH + H_2$$

A hydrogen generating composition in accordance with the present invention preferably also includes a transition metal catalyst, a preferred catalyst being cobalt (II) chloride. Preferably the catalyst is present in an amount of up to 7.5% by wt, typically from 3.7 to 7.1% by wt.

It is preferred that the effect of the second hydride in the composition is to shorten the induction period for the reaction between the complex hydride and water. For instance, in the case where the complex hydride is sodium borohydride and the other hydride is lithium hydride, then the latter hydride will react preferentially with the water, liberating heat and thus raising the temperature of the reaction medium. This in turn activates the hydrolysis reaction of sodium borohydride so that the overall reaction takes place more or less immediately. It is also found that a high yield of hydrogen can be obtained as compared with that in the case where the sole hydride is sodium borohydride and this may be due to the elimination or reduction of the formation of hydrated sodium borate with the mixed hydride system. Also, a high yield of

hydrogen can be obtained as compared with that in the case where the sole hydride is lithium hydride, due to the reduction or elimination of an impervious layer which is formed around the unreacted lithium hydride.

The present invention also provide apparatus for carrying out a chemical reaction in which a hydride containing composition is reacted with water to generate hydrogen, the apparatus comprising a reactor vessel, means for feeding water into said reactor vessel and an outlet for hydrogen, a first part of the interior of the vessel being separated from a second part by means of a porous partition, and said water feeding means includes means for directing water into a plurality of locations within said first part, the hydride containing composition being, in use, located in said first part.

Preferably the apparatus includes a substantially cylindrical reactor vessel having a solid outer wall and an inner, cylindrical, perforated wall. Preferably the ratio of the diameters of the outer and inner walls is from 1.2 to 2 and is preferably about 1.4. More preferably the separation between the inner and outer walls is in the range 5 to 30mm, typically about 10mm.

Preferably there is provided, within said perforated inner wall, a perforated base which is raised from the solid base of the reactor.

In use, a hydride containing composition, such as a composition in accordance with the present invention, is provided in the form of pellets which are located within the inner perforated wall of the vessel. Injection of water on to the pellets causes a reaction to take place in a quasi-liquid phase which is able to flow out of the reactor through the perforated inner wall and in to the space between the inner wall and the outer wall of the vessel. This expansion area or space helps to prevent the compaction which occurs as the product material is formed. Accordingly, unreacted hydride pellets do not become encapsulated in hard residue and thereby inaccessible to water.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will now be described with reference to the accompanying drawings, in which:-

Figures 1 and 2 are graphs illustrating hydrogen generation reactions;

Figure 3 illustrates apparatus, in accordance with the present invention, for carrying out a chemical reaction; and

Figure 4 illustrates further apparatus, in accordance with the present invention, for carrying out the chemical reaction.

PREFERRED EMBODIMENTS

Pellets made in accordance with the present invention comprise the components sodium borohydride, lithium hydride and cobalt chloride. The following table gives typical amounts of cobalt chloride and sodium borohydride in such a composition, based on an amount of *n*% by wt lithium hydride. The table also gives typical ranges for the three components.

Component	% content by wt.	Typical values
Sodium borohydride, $NaBH_4$	92.5 x (100 - *n*)	87.9 - 46.3
Cobalt (II) chloride, $CoCl_2$	7.5 x (100 - *n*)	7.1 - 3.7
Lithium hydride, LiH	*n*	5-50

In a specific example in accordance with the present invention, 200g of pellets consisting of 20% by wt LiH and 6.0% by wt $CoCl_2$ were placed in a reactor. A 6cm^3 "shot" of water was added and a hydrogen generating reaction occurred, liberating about 7 litres of gas. The reactor then idled whilst the liberated hydrogen was consumed by a fuel cell. Approximately 40 minutes after the first shot of water the next shot was added and more hydrogen generated, this process being repeated until the generator shut-down automatically (this occurs when 3 successive injections of water fail to result in hydrogen generation). The total amount of hydrogen liberated was 400.4 litres (stp), a yield of 89% with respect of hydride starting material.

Figures 1 and 2 of the accompanying drawings show how reaction temperature (dotted line) and hydrogen flow rate (solid line) varies with elapsed time from water addition. In Figure 1 hydrogen is generated by the addition of water to pellets comprising sodium borohydride and cobalt chloride. It will be seen that the reaction temperature rises gradually from about 12°C

over a period of about 15 minutes to 50°C. Hydrogen generation is very low until about 14½ minutes have elapsed at which time reactor temperature is about 35°C.

Figure 2 illustrates the effect of including about 20% by wt lithium hydride in the composition. In this case the temperature rises immediately to about 20°C and remains between 20 and about 25°C over a period of about 10 minutes. Hydrogen generation also occurs immediately and is complete within the period of about 1 minute. In addition, increased chemical yield occurred due to the improved control of the system made possible because of the predictability of the reaction.

With a composition in which the only hydride present is lithium hydride, efficient generation of hydrogen is not possible because the reaction with water produces a hard hydroxide (LiOH) which has a greater molar volume than the hydride. Accordingly there is a significant expansion upon reaction and an impervious layer is formed around the unreacted hydride. In a composition according to the present invention the lithium hydride component is effectively diluted so that encapsulation does not occur, while sufficient heat is evolved to activate the sodium borohydride reaction.

Referring to Figure 3 of the accompanying drawings, there is illustrated apparatus for carrying out a chemical reaction in which a hydride containing composition, such as one in accordance with the present invention, is reacted with water to generate hydrogen. The apparatus includes a substantially cylindrical reactor vessel 1 having a solid outer wall 3. The apparatus is provided with a pump (not shown) to feed water into the top of the vessel via inlet pipe 5. Within the vessel 1 inlet pipe 5 terminates in a multi-way injection nozzle 7 which provides a plurality of water outlets (four as shown in Figure 3) allowing water to be downwardly directed into a central portion of vessel 1.

Reactor vessel 1 is also provided with a hydrogen outlet pipe 9 allowing hydrogen to exit from the vessel to a point of use or a storage container.

Reactor vessel 1 is provided with an inner porous or perforated cylindrical wall 11 which is located centrally within the outer wall 3. Perforated wall 11 is provided also with a perforated top 13 and a perforated base 15 which is spaced upwardly from the bottom of the vessel 1.

The diameter of the perforated inner wall 11 is 50mm and the diameter of the outer wall 3 is 70mm. The perforated base 15 is spaced about 10mm above the bottom of the outer wall 3.

As shown in Figure 3, the outlets of injection nozzle 7 are all located vertically above the top 13 of the perforated inner wall 11. In use, a composition in the form of hydride containing pellet 17 is loaded into the space defined by inner wall 11 so that the pellets are located on perforated base 15 (see Figure 3). Water is pumped into the vessel via pipe 5 and is directed into the space defined by perforated wall 11 via the injection nozzle 7. In the case where hydrogen is being generated by the reaction between water and sodium borohydride, the reaction takes place in a quasi-liquid phase which is able to flow away from pellets 17 through the perforated wall to reside in the expansion space created between the perforated walls and the outer wall 3. The unreacted hydride pellets are contained within the mesh tube formed by the perforated inner wall 11. The inclusion of an expansion area reduces the compaction which occurs as the product material is formed. The hydride pellets do not become encapsulated in a hard product residue and accordingly they remain accessible upon subsequent water addition.

Figure 4 illustrates how several modules 21 (each of which may be similar to the apparatus shown in Figure 3) may be assembled inside a single pressure vessel 23 to form a hydrogen generator capable of operating for *n* times the life of a single module, where *n* is the number of modules. The apparatus is provided with a water pump 25 which draws water from a water reservoir 27. The water is supplied by pump 25 to a switching valve 29 which allows the water to be directed to a selected one of the modules 21. The hydrogen which is generated may be supplied via line 31 to a fuel cell.

A controller 33 receives data from pressure and temperature sensors 35, 37 attached to line 31 and sends instructions to water pump 25 and switching valve 29.

An ammonia scrubber 39 is included to remove trace ammonia that is produced during the reaction between lithium hydride and water as the fuel cell is poisoned by ammonia. A particulate filter 41 is included to remove particles from the gas stream to extend the lifetime of the fuel cell.

CLAIMS

1. A hydrogen generating composition comprising two hydrides both capable of reaction with water to produce hydrogen, one of said hydrides being a complex hydride of a Group IA element and a Group IIIB element, whereby the presence of the other of said hydrides results in the reaction with water of the composition being modified compared with that of the complex hydride alone with water.

2. A composition according to Claim 1 wherein the complex hydride is present in the composition in a relatively major amount compared with the other of said hydrides.

3. A composition according to Claim 1 or Claim 2 wherein the complex hydride is sodium borohydride.

4. A composition according to any of the preceding claims wherein the other hydride is lithium hydride.

5. A composition according to any of the preceding claims wherein the complex hydride is present in the amount of from 45 % to 90% of the total weight of the composition.

6. A composition according to any of the preceding claims wherein the other hydride is present in the amount of from 5 to 20% by weight of the total composition.

7. A composition according to any of the preceding claims wherein the other hydride acts to reduce the time of initiation of hydrogen generation.

8. A composition according to any of the preceding claims and including a transition metal catalyst.

9. A composition according to Claim 8 wherein the catalyst is cobalt (II) chloride.

10. A composition according to Claim 8 or Claim 9 wherein the catalyst is present in an amount of up to 7.5% by wt of the total composition.

11. A hydrogen generating composition comprising two hydrides and substantially as herein described.

12. A hydrogen generating composition substantially as specifically described herein.

13. Apparatus for carrying out a chemical reaction in which a hydride containing composition is reacted with water to generate hydrogen, the apparatus comprising a reactor vessel, means for feeding water into said reactor vessel and an outlet for hydrogen, a first part of the interior of the vessel being separated from a second part by means of a porous partition, and said water feeding means including means for directing water into a plurality of locations within said first part, the hydride containing composition being, in use, located in said first part.

14. Apparatus for carrying out a chemical reaction and substantially as described with reference to Figure 3 or Figure 4 of the accompanying drawings.

15. Apparatus according to Claim 13 substantially as herein described.

hydrogen

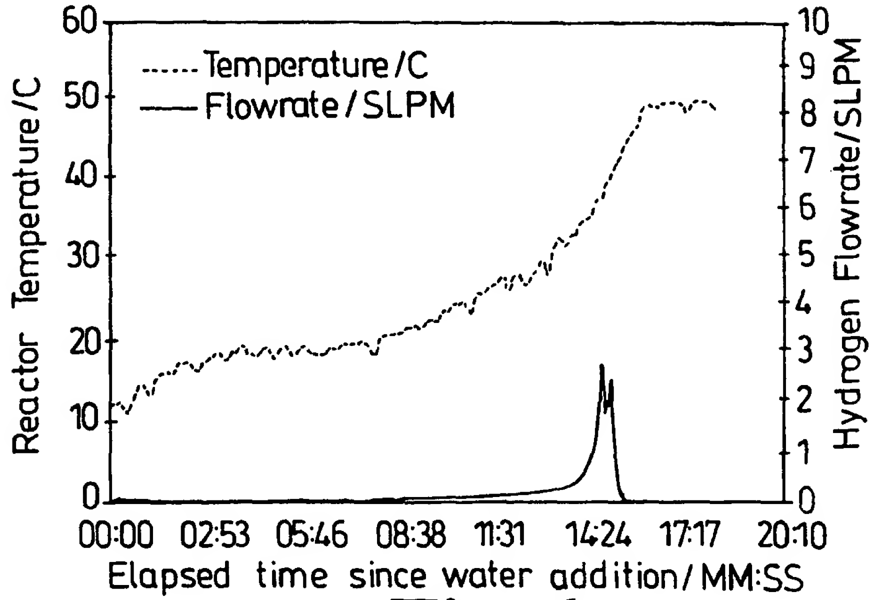

Fig. 1

Hydrogen generation by the addition of water to sodium borohydride/cobalt chloride pellets.

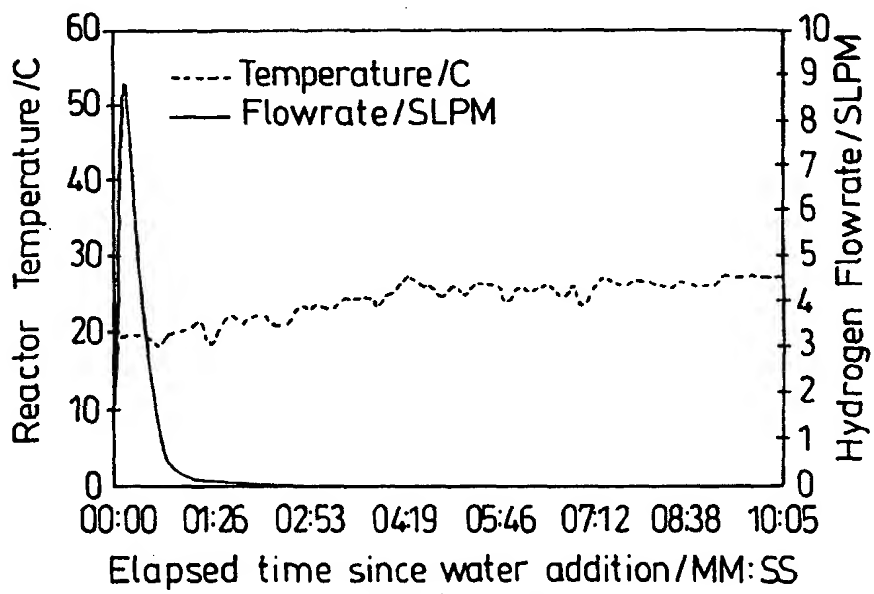

Fig. 2

Hydrogen generation by the addition of water to sodium borohydride /cobalt chloride pellets containing 20% by wt. lithium hydride.

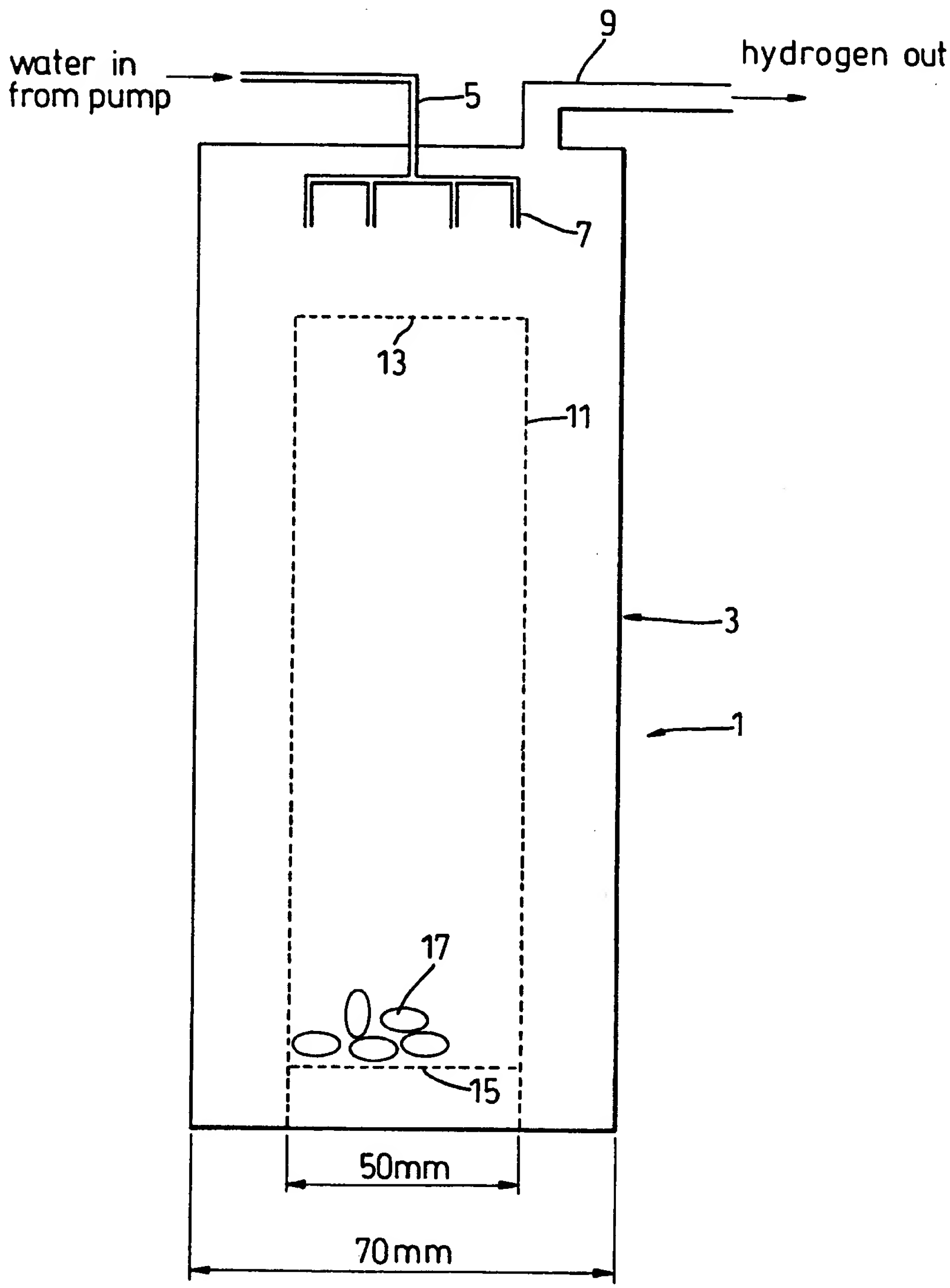

Fig. 3

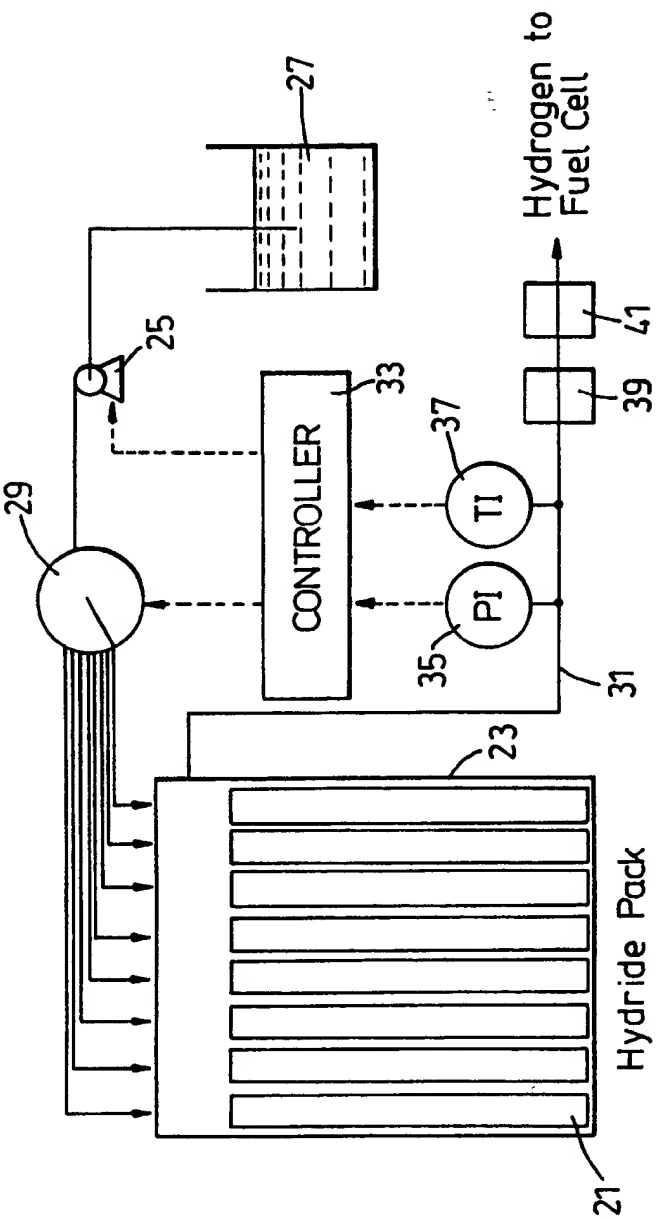
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Fig. 4